

METAL-METAL OXIDE ELECTRODES.

PART I. STUDIES IN TUNGSTEN AND MOLYBDENUM ELECTRODES.

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INTRODUCTION.

The determination of hydrogen-ion concentration of alkaline solutions, particularly those containing substances that render the hydrogen electrode useless, has always been a problem of some difficulty. Metal-metal oxide electrodes have been used by many workers in place of hydrogen electrode. Uhl and Kestranek (*Monatsh.*, 1923, 44, 29) proved that a silver electrode dipping in a suspension of Ag_2O could be used in place of Hg/HgO (yellow) used by Allmond (*Zeit. Electrochem.*, 1910, 16, 254), but the electrode could only be used in the absence of chloride ions. This led them to find a convenient type of electrode, which on one hand was not complicated in construction, and was not as easily polarisable as a hydrogen electrode, and on the other hand could be used, in contrast to the silver and mercury electrodes, in the presence of chlorides and ammonium salts. According to Uhl and Kestranek the metal to be used should fulfil the following conditions:

(1) The metal should be sufficiently noble, so that it does not dissolve in dilute acids.

(2) It must give correct concentration with respect to the corresponding hydroxyl ions.

(3) The oxide must have a very little solubility product and must be of amphoteric character.

Antimony metal appeared to satisfy the above conditions and after a successful use, they found that at the neutralization points, sharp potential jumps in electrometric titration of acids and bases were obtained with an indicator electrode of bare stick of antimony without any addition of oxides.

In general it can be said that any metal could be suitable for determining end points in the titration of acids and bases, which developed a sufficiently high electromotive force in acid alkali chain: Metal | acid | alkali | Metal.

Closs and Kahlenberg (*Trans. Electrochem. Soc.*, 1928, 54, 369) and later Holt and Kahlenberg (*Ibid.*, 1930, 57, 361) have studied various metallic pairs for the electrometric titrations. They

found that the difference in the potential developed by a metal in an acid solution and that in a basic solution, is larger in the case of tungsten, platinum, antimony and molybdenum and that these can be used as indicator electrodes. In the case of other metals the difference is comparatively small. According to them the most serviceable pairs for acid alkali titrations are tungsten-graphite, antimony-graphite and tungsten-silver.

Furman and Low Jr. (*Jour. Amer. Chem. Soc.*, 1933, 55, 1310) have also used the pairs tungsten-nickel, tungsten-calomel and nickel-calomel for obtaining the end points in the electrometric titration of acids and bases.

In a preliminary study of this problem, the authors have studied the following metals: tungsten, antimony, molybdenum, bismuth, tantalum, tantalum coated with a blue oxide, platinum, silver, nickel, copper, cadmium and cobalt at different pH values. Clark and Lub's standard buffer mixtures were used. All the measurements were done against a saturated calomel electrode and the buffer solutions were checked either against hydrogen or quinhydrone electrode. A record of results is shown in Fig. 1.

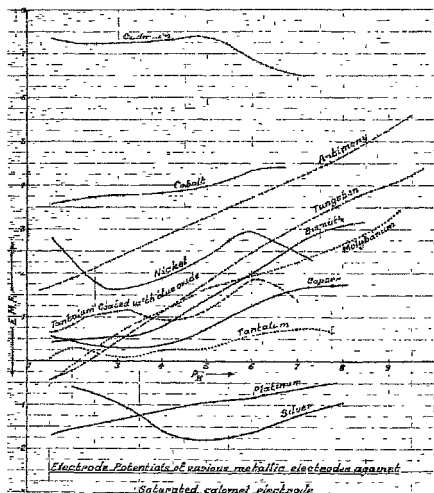


FIG 1.

It was observed that tungsten, antimony and molybdenum showed a good pH dependency and a straight line relationship was obtained between pH 3 to pH 8.

Bismuth showed a nearly linear relationship of electromotive force with pH between 5 to 7 which was in good agreement with the values obtained by Metha and Jatkar (*This Journal*, 1935, 18A, 109).

In the case of tantalum, platinum, silver, nickel, copper, cadmium and cobalt no definite relationship was obtained. The electrodes seemed to fluctuate very much and a change of E.M.F. was observed with respect to time. Cadmium and cobalt showed a nearly constant E.M.F., *viz.*, $0.73 \pm .01$ and $0.37 \pm .01$ volts between pH 2 to pH 6 respectively.

Platinum and silver developed an E.M.F. which was negative to that developed by other metals. The following table (I) gives the range of pH over which the various metals show a straight line relationship between E.M.F. and pH.

TABLE I.

Metal	pH range	
	Theoretical relationship	Straight line relationship
Tungsten	3.5-5.5	3-8
Antimony	2-8	2-8
Molybdenum	6.5-7.5	{ 2-5 6-8
Platinum	1.5-8
Silver	6-8
Nickel	3.5-5	3.5-5
Copper	5-6	5-6

The results show that tungsten, antimony and molybdenum can be used as indicator electrodes with a great advantage: the rest of the metals do not serve as good indicator electrodes because they show a very small difference of potential with increasing pH. However, such unsatisfactory electrodes when paired with a good indicator electrode may make an excellent couple for titration purposes. A still better couple obviously would be obtained if two suitable indicator electrodes were used, each showing an appreciable change of potential at the end point but developing a potential in opposite directions.

A couple consisting of two indicator electrodes which increase in potential in the same direction as titration proceeds, would obviously be an unsatisfactory couple. Accordingly, the most serviceable pairs for acid alkali titration, will be tungsten-silver, tungsten-platinum, antimony-silver, antimony-platinum, molybdenum-silver and molybdenum-platinum.

Holt and Kahlenberg (*loc. cit.*) have done extensive work in this field and have classified the various metals in order of the amphoteric nature of the oxides.

Of the three electrodes (*viz.*, tungsten, antimony, molybdenum) the exhaustive study of the antimony electrode has been carried out by Kolthoff and Hartog (*Rec. Trav. Chim. Pays-Bas.*, 1925, **44**, 113), Park and Beard (*J. Amer. Chem. Soc.*, 1932, **54**, 856), various other workers and more recently by Metha and Jatkar (*This Journal*, 1935, **18A**, 85). The work of the various authors has shown that the behaviour of the metallic electrodes is primarily due to the formation of insoluble hydroxide on their surfaces.

The theory of the metal-metal oxide electrode is as follows:—

The E.M.F. of the metal-metal oxide electrode depends on the concentration of the ions that the metal can deliver. In the case of tetravalent tungsten (W^{4+}) the E.M.F. of the electrode in contact with the solution is

$$E = E_w + RT/nF \log_e (W^{4+}) \quad \dots (I)$$

where $E_w = RT/nF \log_e (P/W^{4+})$ P being the Nernst solution pressure. In the case of tetravalent tungsten $n = 4$ and the term RT/F being 0.05915 at 25° the equation (I) reduces to

$$E = E_w + \frac{0.05915}{4} \log (W^{4+}) \text{ at } 25^\circ \quad \dots (II)$$

In solutions in which the oxide of tungsten is insoluble the concentration (W^{4+}) is governed by the solubility product

$$S = [W^{4+}] \times [OH^-]^4$$

$$\text{and therefore } [W^{4+}] = \frac{S}{[OH^-]^4} = \frac{S}{K_w^4} \times [H^+]^4$$

where K_w is the ionic product of water.

$$\begin{aligned} \text{Therefore } E &= E_w + \frac{0.05915}{4} \log \frac{S}{K_w^4} \times [H^+]^4 \\ &= E_w + \frac{0.05915}{4} \log \frac{S}{K_w^4} + 0.05915 \log [H^+] \quad (III) \\ &= E_0 (\text{constant}) - 0.05915 \text{ pH} \quad \dots \quad (IV) \end{aligned}$$

The equation IV is independent of the valency of the metal and it appears, on theoretical grounds, that a metal electrode dipping in a solution containing some of its oxide so as to saturate the solution with the hydroxide, should set up a potential depending upon the concentration of hydrogen ions and some constant function, involving both electromotive activity of the metal and the solubility product of its hydroxide. Its potential should, therefore, alter by 0.05915 volts for a change of one pH unit in hydrogen-ion concentration. From the equation III, we see that for the above relation to hold good, the value of the solubility product S should remain constant and small in magnitude. Higher and varying values of S will change the value of E_0 and the E.M.F. recorded will not be a correct function of pH. The above linear relationship is regarded as the ideal case; experimental complications arise due to the solubility of the oxide, its dependence upon the size of its grain and sluggishness with which it enters into equilibrium, when undergoing changes in hydrogen-ion concentrations. These factors affect the constancy of E_0 , but as these fluctuations are often themselves functions of pH of the solution, it is possible to construct calibration curves connecting pH values and observed potentials in the case of certain metals.

The metal-metal oxide electrodes are, in fact, oxygen electrodes in which the precise pressure of oxygen is determined by the tendency of the oxide to dissociate into free oxygen and the metal at a particular temperature. Assuming for the present that the oxygen electrode is reversible, the difference in potential which exists between two oxygen electrodes having different oxygen pressures immersed in solution whose oxygen ions exert an osmotic pressure of P atmospheres, could be accounted for, on the ground that the oxygen ions at the surfaces of the two electrodes would have different electrolytic solution pressures.

In a cell, if the pressure of one oxygen electrode was equal to one atmosphere, and that of the other as π atmospheres, then the E.M.F. of the cell would be

$$\text{E.M.F.} = \frac{RT}{4F} \log \frac{1}{\pi} = \frac{0.05915}{4} \log \frac{1}{\pi} \text{ at } 25^\circ \text{C.}$$

If, therefore, a metal-metal oxide electrode be substituted for the oxygen electrode of pressure π where π is the dissociation pressure of oxide, then the E.M.F. will be = $\frac{0.05915}{4} \log \frac{1}{\pi}$.

From this it is possible to calculate the dissociation of the oxide of the metal used as an electrode. Britton has observed that in the case of silver-silver oxide electrode the value of the vapour pressure of silver oxide is in good agreement with that observed by G. N. Lewis (*J. Am. Chem. Soc.*, 1906, 28, 158). By using the value, 5×10^{-4} , given by Lewis, he obtained 1.216 volts as the value of oxygen-hydrogen cell, which is a few millivolts lower than the extrapolated value of Nernst and Wartenberg, *viz.*, 1.226 volts at the temperature.

Allmond (*loc. cit.*) has studied the mercury-mercuric oxide electrode for the measurement of pH in alkaline solutions and found it to be always 0.925 volt more positive at 18° than the corresponding hydrogen electrode. From this he calculates 6×10^{-22} atmosphere as the dissociation pressure of mercuric oxide at 18° C.

The antimony electrode (Metha and Jatkar, *loc. cit.*) is found to be 0.277 volt more positive than the corresponding hydrogen electrode. By taking the potential of oxygen-hydrogen cell as 1.226 volts at that temperature, the dissociation pressure of antimony tetroxide is found to be 1×10^{-64} atmosphere at 25° C.

Many other metal-metal oxide electrodes have been studied. Copper-cupric oxide electrode has been found to be unsatisfactory by Britton (*J. Chem. Soc.*, 1925, 127, 2796). Heyrovsk'y (*J. Chem. Soc.*, 1920, 117, 35) has studied the aluminium electrode and proved the action taking place at the surface of the electrode was due to the thin film of aluminium hydroxide which has a very small solubility product, *viz.*, 10^{-33} .

In this investigation, we have studied the behaviour of bare tungsten and molybdenum wires for the determination of hydrogen-ion concentrations and for differential titration of acids and bases.

Many workers have used the bare tungsten wire electrode for the determination of pH of solutions. Baylis (*Ind. Eng. Chem.*, 1923, 15, 852) was the first to use the tungsten filament of an arc lamp for measuring the pH of river water over the range 6.5 to 8.6 units, but his data reveals a difference of 0.09 volts in E.M.F. for each pH unit change. He has patented a form of the electrode (U.S.P. 1,727,094/1929). Parker (*Ind. Eng. Chem.*, 1925, 17, 737) studied the tungsten electrode in contact with oxides of various metals, in buffer solutions ranging from pH 4 to 9, and concluded that the electrode coated with manganic oxide was the most satisfactory. Holven (*Ind. Eng. Chem.*, 1929, 21, 965) found that bare tungsten wire electrodes are capable of yielding

accurate pH measurements of sugar solutions. He coated the wire with an oxide film by immersion in a solution of normal sodium phosphate for two days, followed by a further immersion for two days in a solution of a substance which was subsequently to be tested. The values of E.M.F. obtained by him were different for different solutions, thus showing that the electrode did not keep its calibration for a long time. He got a difference of 0.04 volts per unit pH change. Britton and Dodd (*Jour. Chem. Soc.*, 1931, 829-36) have investigated the behaviour of both wire and filament of tungsten over a pH range 2-12 (*cf.* Fig. 3), using for calibration the modified Prideaux-Ward universal buffer mixture. They studied the electrode after anodic oxidation in dilute sodium hydroxide and found that the results obtained were not satisfactory. Their values of E_0 (*cf.* Fig. 3) changed from 0.32 volts at pH 2 to 0.54 volts at pH 12, the average difference of E.M.F. per unit pH change being about 0.043 volts. The electrode did not keep its calibration for a period longer than a day. They have found the electrode to be satisfactory for the titration of acetic, boric, phosphoric, maleic and hydrazoic acids. Iofa and Petrov (*Zavodaskaya Lab.*, 1934, 4, 728) have measured the potential of tungsten electrode over the pH range 4-10.

EXPERIMENTAL.

(A) TUNGSTEN ELECTRODE.

The electrode used was a tungsten wire about 20 cm. long and 1 mm. in thickness, dipping in the solution to a depth of about 4 to 5 cm. The electrode was polished bright with a fine grade emery paper and washed with distilled water before the commencement of each experiment.

The electromotive force was measured on a Tinsley's vernier type potentiometer. A saturated calomel half-cell was used as a reference electrode. The pH values of all buffer mixtures were checked against either quinhydrone or hydrogen electrode. The measurements were made at room temperature and calculated for 25°.

In earlier experiments an electrode coated with a metallic oxide as used by Britton and Dodd was tried, but the results obtained were not satisfactory.

The first set of experiments were done in an open beaker, and Clark and Lub's standard mixtures were used as buffers. The results are given in the following table (II).

TABLE II.

Calomel temp: 25° - 25.4°.

Cell temp.	Quinhydrone E.M.F.	pH	Tungsten E.M.F.	- E' in volts corrected for 25°	- E ₀ in volts with reference to normal hydrogen electrode at 25°
23.2	0.3196	2.30	- 0.0310	0.1668	0.4126
„	.2776	3.00	- 0.0211	.1569	.4027
„	.2354	3.73	+ 0.0334	1869	.4327
23.4	.2188	4.01	.0475	.1895	.4353
23.2	.1696	4.86	.0899	.1976	.4434
23.5	.1217	5.66	.1120	.2225	.4683
„	.0689	5.56	.1473	.2407	.4865
23.6	.0075	7.60	.2134	.2356	.4814

Another set of experiments were carried out in an atmosphere of hydrogen. A special apparatus (Fig. 2) was fitted up for the purpose. A cylindrical vessel was fixed with a rubber cork having a number of holes to admit the various elements, *viz.*, hydrogen,

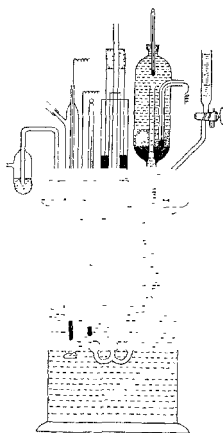


FIG. 2.

calomel, and tungsten electrodes, gas trap, thermometer, the burette tip and a mechanical stirrer passing through a mercury seal. The calomel half-cell was connected with a bridge having a ground-glass stopper (to prevent diffusion) at one end, which dipped in the buffer solution, while the calomel half-cell was introduced through the upper end.

The measurement was based on the neutralization of Britton and Robinson's Universal Buffer solution with sodium hydroxide. 100 c.c. of the former were titrated with 0.089 N alkali. The hydrogen gas was allowed to bubble through the solution for about 3 to 4 hours before starting measurements. There was no polarization of the electrode and a steady reading was usually obtained within 1-2 minutes after addition of alkali. The results are given in Table III.

TABLE III.

(Calomel temp. 23.5° - 24.1°.)

Cell temp.	c.c. of NaOH	Hydrogen calomel E.M.F.	pH	Tungsten E.M.F.	- E in volts corrected for 25°	- E ₀ in volts with reference to normal hydrogen electrode at 25°
20.2	0	0.3335	1.48	0-- -0.479	0.1263	0.3821
20.5	5	.3368	1.54	-- -0.501	.1422	.3880
20.7	10	.3408	1.61	-- -0.531	.1486	.3944
20.9	15	.3449	1.68	-- -0.548	.1560	.4018
21.1	20	.3497	1.76	-- -0.558	.1613	.4071
21.4	25	.3545	1.84	-- -0.568	.1668	.4126
21.5	30	.3607	1.89	-- -0.565	.1726	.4184
21.7	35	.3664	2.07	-- -0.563	.1780	.4244
21.8	40	.3739	2.13	-- -0.555	.1851	.4309
22.0	45	.3828	2.32	-- -0.534	.1921	.4379
22.1	50	.3946	2.32	-- -0.485	.1989	.4447
22.2	55	.4230	2.82	-- -0.375	.2061	.4519
22.3	60	.4405	3.30	-- -0.133	.2096	.4554
22.5	65	.4659	3.73	+ -0.053	.2161	.4619
22.6	70	.4835	4.04	. -0.268	.2143	.4601
22.7	75	.4962	4.25	. -0.376	.2138	.4596
22.8	80	.5064	4.42	. -0.477	.2161	.4619
22.9	85	.5160	4.58	. -0.581	.2131	.4589
23.0	90	.5275	4.78	. -0.664	.2165	.4623

TABLE III (Contd.).

Cell temp.	c.c. of NaOH	Hydrogen calomel E.M.F.	pH	Tungsten E.M.F.	- E' in volts corrected for 25°	- E ₀ in volts with reference to normal hydrogen electrode at 25°
23-1	95	-5397	5-01	-0873	-2066	-4524
..	100	-5520	5-19	-0994	-2075	-4533
23-2	105	-5666	5-49	-1116	-2096	-4554
23-3	110	-5849	5-74	-1329	-2086	-4544
23-4	115	-6041	6-08	-1534	-2065	-4523
23-5	120	-6245	6-43	-1755	-2066	-4524
23-6	125	-6458	6-78	-1975	-2041	-4499
23-7	130	-6690	7-18	-2235	-2033	-4491
..	135	-6936	7-59	-2392	2096	-4554
..	140	-7155	7-97	-2631	-2083	-4541
23-8	145	-7337	8-27	-2787	-2095	-4553
..	150	-7471	8-50	-2893	-2106	-4564
..	155	-7585	8-69	-3023	-2115	-4573
23-9	160	-7692	8-88	-3128	-2114	-4572
..	165	-7801	9-07	-3215	-2149	-4607
24-0	170	-7908	9-25	-3320	-2147	-4605
..	175	-8027	9-44	-3421	-2148	-4606
..	180	-8119	9-60	-3503	-2184	-4642
24-1	185	-8444	10-13	-3687	-2304	-4762
..	190	-8756	10-66	-3937	-2365	-4823
24-2	195	-8946	10-98	-4090	-2402	-4860
..	200	-9072	11-19	-4216	-2446	-4904
24-3	205	-9155	11-34	-4256	-2442	-4900
..	210	-9222	11-48	-4318	-2435	-4893
..	215	-9271	11-53	-4358	-2458	-4916
..	220	-9316	11-64	-4400	-2460	-4918
24-4	225	-9357	11-67	-4459	-2443	-4901
..	230	-9384	11-72	-4493	-2447	-4905
..	235	-9413	11-77	-4521	-2433	-4891
..	240	-9443	11-83	-4556	-2436	-4894
..	245	-9467	11-85	-4581	-2433	-4891
24-5	250	-9479	11-87	-4606	-2422	-4880

Experiments were also carried out to study the behaviour of tungsten electrode by bubbling oxygen and air. The electrode gave potentials which have theoretical slopes at certain pH ranges as shown in the following table:

pH range	1.6 to 2.5	5.8 to 7.2	10.2 to 11.5
E_0 Oxygen ..	0.261	0.424	0.525
E_0 Air ..	0.286	..	0.525
E_0 Hydrogen ..	0.437 0.490	from pH 2.8 to 9.4 .. pH 10.8 to 12	

DISCUSSION OF RESULTS.

In Tables II and III the observed values of E.M.F. of tungsten electrode against saturated calomel have been reduced to 25° and plotted against their respective pH values in Fig. 3 (a). According to theoretical relationship $E = E_0 - 0.0591 \text{ pH}$, E_0 ought to be a constant quantity and the slope of the line should be 0.0591 at 25°. From the graph (Fig. 3) it is seen that this relationship holds

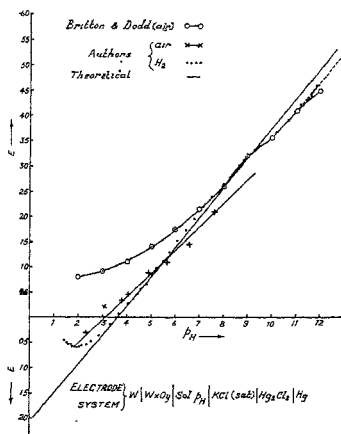


FIG. 3 (a).

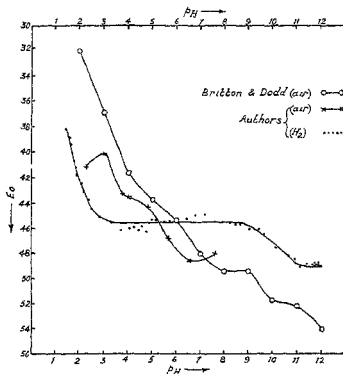


FIG. 3 (b).

good over a pH range 2.8 to 9.4 provided the electrode is used in an atmosphere of hydrogen. At pH 3.5 the value of the observed E.M.F. is zero. The extrapolated curve cuts the y-axis at the value -0.212 , and the value of E.M.F. against saturated calomel at any pH value, is given by the equation $E_{(obs.)} = -0.212 + 0.0591 \text{ pH}$.

The last columns in Tables II and III show the values of E_0 , the potentials of tungsten electrode against normal hydrogen. The values are plotted in Fig. 3 (b). In the case of measurements in open vessel, these values increase with pH and remain nearly constant between pH 3 to 5. Beyond these limits the electrode does not function as a theoretical electrode, though the linear relationship still holds good and the hydrogen-ion concentrations at various points can be calculated with the help of a previously obtained calibration curve. The values of E_0 obtained by Britton and Dodd (*Jour. Chem. Soc.*, 1931, 829-35) are also plotted in Fig. 3 (b); their values are found to be slightly different from those obtained by the author.

In the other set of experiments (in hydrogen atmosphere) E_0 remains constant at 0.457 and 0.490 over a range of pH 2.8 to 9.4 and 10.8 to 12 respectively.

Experiments were carried out to measure the temperature coefficient of the tungsten electrode. The E.M.F. of the cell Pt; H_2 | solution pH | tungsten wire at two different temperatures was measured. The cell used was of the same type as described in Fig. 2. The results are given in the following table:

pH	Time	Temp.	E.M.F.
4.04	9-55 A.M.	25° C.	0.4053
	10-25 "	50° C.	.3758
	10-55 "	25° C.	.4046
5.30	11-55 A.M.	25° C.	0.4082
	12-25 P.M.	50° C.	.3733
	12-55 "	25° C.	.4040
6.70	1-50 P.M.	25° C.	0.4073
	2-20 "	50° C.	.3794
	2-50 "	25° C.	.4025

The average value of E_0 at 25° C. = 0.4063 volts

" " " " E_0 at 50° C. = .3762 "

From the above results the value of the temperature coefficient of tungsten electrode is 0.00116 volts per degree.

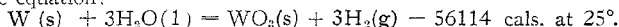
In the following table (IV) the values of free energy and heat content calculated from the above values of E_0 for the formation of various possible oxides from the metal, are given:

TABLE IV.

E_0 at 25°	Oxide	Free energy of formation	Heat of formation in calories	
			Calculated	Observed
0.4053 0.4570	WO ₂	75.70	129.80 129.00	136.2 ¹ , 127.9 ² , 82.6 ³ , 131.00 ⁴
0.4053 0.4570	WO ₃	113.57	194.42 193.50	195.4 ⁵ , 194.9 ⁶ , 199.9 ⁷ , 196.3 ⁸ , 192.6 to 196.2 ⁹
0.4053	W ₂ O ₅	180.28	327.30	283.7 ³ , 318.4 ²

1. L. Wohler and Gunther, *Zeit. Electrochem.*, 1923, **29**, 276.
2. J. A. Van Lempt, *Zeit. anorg. Chem.*, 1923, **126**, 186, 226.
3. H. Alterthum and F. Koref, *Zeit. Electrochem.*, 1925, **31**, 508.
4. Wartenberg and Moehl, *Zeit. Phys. Chem.*, 1927, **128**, 439.
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8. Mixer, *Amer. Jour. Science*, 1908, (4) **27**, 125.
9. Weis, *Zeit. anorg. Chem.*, 1910, **65**, 334

The decrease in free energy change at each temperature was calculated from the value of nFE at each temperature and is expressed by the equation:



The equation for the free energy of formation of water at 25° is $3H_2(g) + 3/2 O_2(g) = 3H_2O(l) + 169680$ (Lewis and Randall, *Thermodynamics*, p. 485). Adding the two equations we get $W(s) + 3/2 O_2(g) = WO_3(s) + 113570$ cal. This is the free energy of formation of WO₃ from metallic tungsten and oxygen at 25°.

The heat content of the oxides is calculated by substituting the decrease in free energy values for each temperature in Gibbs-Helmholtz equation, integrated on the assumption that the heat content change ΔH is constant over a small range 25° to 50°:

$$-\frac{\Delta F_2}{T_2} - \frac{-\Delta F_1}{T_1} = \Delta H \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

The value obtained for $-\Delta H$ is the heat content decrease at 37.5° . Combining this value with that of heat content of water at 25° which is -3×68270 (Lewis and Randall, *Thermodynamics*, First Edition, p. 477) for $3H_2O(l)$, we get the value for the heat content of different oxides which is given in the 5th column of Table V. The relative thermochemical data obtained by different workers for the heat of formation for various oxides is given in the last column. The calculated values agree more with the data obtained by various workers for WO_3 than for WO_2 . The results indicate the existence of tungsten trioxide on the upper layers of the surface on the wire.

The existence of the tungsten tri-oxide on the surface of the metal is probable as it is formed by the oxidation of the metal in air. It is possible that a certain portion of the oxide might have got dissolved on the surface before cooling.

From the equation $E = E_0 - 0.059 \text{ pH}$, it is evident that the theoretical behaviour of the electrode entirely depends on the constancy of E_0 , which in turn depends on the solubility product (S) of the oxide. As already mentioned, it is essential that the oxide should be of an amphoteric character to enable the electrode to function over a wide range of pH. This condition is satisfied by tungsten trioxide to some extent.

The electrode is found to be 0.405 volts more positive than the corresponding normal hydrogen electrode in the same solution. Taking the value of E.M.F. of oxygen-hydrogen cell as 1.226 volts at $25^\circ C.$, the value of dissociation pressure of WO_3 as calculated is 4×10^{-36} atmosphere.

(b) MOLYBDENUM ELECTRODE.

A polished molybdenum wire about 10 cm. long and 1 mm. in thickness was used for measurements of pH. The method of procedure was the same as that followed in the case of tungsten electrode. Britton and Robinson's Universal buffer mixtures were used.

The values of E.M.F. of molybdenum electrode against calomel and values of E_0 for the same electrode are given in Tables V and VI

TABLE V.
Measurements carried out in an open vessel.
 Calomel temp. = 29° C.

Cell temp.	0.1057 N NaOH	Hydrogen calomel E.M.F.	pH	E.M.F. observed	- E' in volts	- E _o observed in volts with respect to normal hydrogen electrode
25.4	0	0.3416	1.67	0.0093
..	20	.3639	1.04	.0042	0.1053	0.3481
..	40	.4019	2.68	.0486	.1080	.3508
..	60	.4896	4.16	.1051	.1387	.3815
25.5	80	.5324	5.22	.1544	.1609	.4037
..	100	.6182	6.34	.1816	.1900	.4328
25.4	120	.6605	7.05	.2152	.2077	.4505
25.5	140	.7379	8.35	.2565	.2310	.4738
25.6	160	.7955	9.32	.3037	.2557	.4985
..	180	.8778	10.72	.3686	.2667	.5095
..	200	.9119	11.30	.4045	.2653	.5081

TABLE VI.
Measurements carried out in an atmosphere of hydrogen.
 Calomel temp. 23.5° - 24.5° C.

Cell temp.	0.130 N NaOH	Hydrogen calomel E.M.F.	pH	E.M.F. observed	- E' in volts	- E _o observed in volts with respect to normal hydrogen electrode
22.8	0	0.3244	1.31	- 0.0115	0.0967	0.3437
23.2	30	.3610	1.94	+ .0214	.0977	.3366
23.4	50	.4163	2.88	.0612	.1086	.3555
23.6	65	.4891	4.12	.1102	.1313	.3781
..	75	.5171	4.60	.1254	.1448	.3915
23.8	85	.5442	5.06	.1450	.1534	.4001
24.1	100	.6059	6.10	.1999	.1604	.4069
24.2	110	.6538	6.91	.2403	.1681	.4144
24.3	120	.7055	7.79	.2785	.1809	.4273
..	140	.7664	8.83	.3176	.2027	.4492
24.5	150	.7889	9.20	.3308	.2117	.4580
24.6	160	.8154	9.65	.3564	.2154	.4616
..	170	.8686	10.54	.4011	.2223	.4685

and shown in Fig. 4. It is observed that the electrode shows a theoretical slope over three pH ranges as shown in the following table:

Molybdenum electrode	pH ranges		
In hydrogen	1.5 to 2.7	5 to 7	9.5 to 11.7
In air	2 to 2.7	6.3 to 7.2	9.5 to 11.5

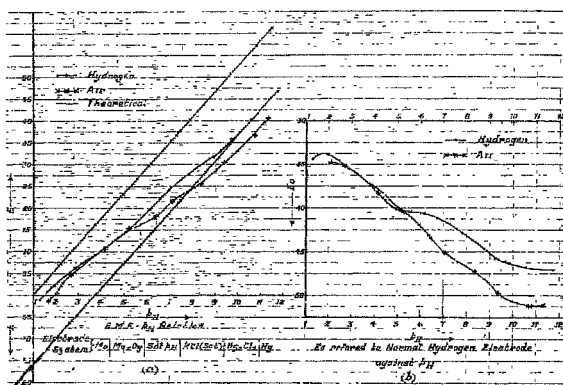


FIG. 4.

Straight line relationship between pH and E.M.F. is observed over a pH range 2 to 11 and the pH at any point can be calculated from the calibration curve which is given by the equation $E = -0.06 + 0.043 \text{ pH}$.

The steady increase of potential with increasing pH indicates the existence of various oxides and sub-oxides of molybdenum having different solubility products.

During the course of work it was observed that molybdenum wire became coated with a pale brown film of oxide as the pH of the solution was increased and that the electrode got oxidised more readily than tungsten electrode.

SUMMARY.

1. The behaviour of polished tungsten and molybdenum wire electrodes has been studied over a pH range 2-12 in an atmosphere of hydrogen. It has been shown that tungsten electrode gives a theoretical relationship of pH and E.M.F. over a range of pH 2.8 to 9.4, while molybdenum, over a short range from pH 5 to 7.

2. Experiments have also been made in atmosphere of air and oxygen. when the electrodes deviated very much from the theoretical relationship.

3. Temperature coefficient of the system $Pt; H_2 | \text{solution pH} || W_xO_y | W$ has been measured and the values for free energy and heat of formation of various oxides calculated. The calculated data agrees well with the heat of formation of tungsten trioxide on the surface of the metal.

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[Received, 10-10-1938.]